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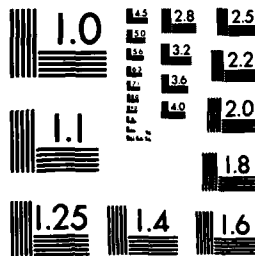
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Photodegradation of Segmented Polyurethanes Based
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by

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) The photodegradation of polyurethanes based on aromatic diisocyanates is shown to be dependent on the physical state of the polymer. For simple polyurethanes based on p,p'-diphenylmethane diisocyanate (MDI) and a single diol, films with low crystallinity and high flexibility degrade quite rapidly upon exposure to UV radiation. In the case of segmented polyurethanes based on MDI and more than one diol, the extent and mechanism of photolytic decomposition is dependent on the hard segment (MDI-1,4-butanediol) content in the polymer. As the degree of hard segments in the polymer increases both the percent crosslinked gel and discoloration generated upon photolysis decreases dramatically. In addition, formation of the ortho photo-Fries rearrangement product increases with an increase in the molecular weight of the poly(ethylene oxide) soft segment.			
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Photodegradation of Segmented Polyurethanes Based on Aromatic Diisocyanates

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Introduction

Polyurethanes derived from aromatic diisocyanates are an important class of polymers; however, due to sensitivity to photolytic degradation their use is severely restricted in coatings applications. This is particularly true when outdoor exposure is expected. Marked changes in physical properties and severe discoloration readily occur after only limited exposure to light. In many instances this dictates the use of the more costly aliphatic diisocyanate based polyurethanes.

Two major mechanisms have been proposed to explain discoloration and mechanical property loss of aromatic diisocyanate based polyurethanes upon photolysis. The first involves quinone-imide type chromophores (1-7). The second implies a photo-Fries rearrangement (8) which is generated by an initial N-C bond cleavage of the carbamate group. Interestingly, Gardette and Lemaire (9-11) claim that the photodegradation proceeds by both mechanisms, depending on the excitation wavelength of the photolysis source. They propose that photolysis with light of wavelength below 340 nm affords the ortho photo-Fries rearrangement product while photolysis above 340 nm results in peroxide formation via a photooxidation process. Despite a widespread research effort, the photodegradation of aromatic diisocyanate based polyurethanes remains somewhat obscured.

One of the primary questions of polyurethane photochemistry, which heretofore has received little or no attention, deals with the effect of the polymer physical state on the degradation mechanism. This is no moot point since not all polyurethanes used in coatings applications have the same physical state. This paper addresses the effect of polymer physical structure and local environment on the photolytic degradation of aromatic diisocyanate based polyurethane films. In particular, results from photodegradation studies of simple polyurethanes made from MDI and a single aliphatic diol as well as segmented polyurethanes based on MDI, a short-chain aliphatic diol, and high molecular weight polyols are presented which demonstrate that both crystallinity and local environment are important in the photolysis process.

Experimental

Methylene 4,4'-diphenyldiisocyanate (MDI-Mobay) was recrystallized before use. Diols (Aldrich) used in polyurethane preparation were either distilled or recrystallized from 1,2-dichloroethane. Poly(ethylene oxide) (PEO) (Aldrich) and poly(tetramethylene oxide) (PTMO) (Polyscience) were dehydrated under a rough vacuum at 50 C for 1 day. The polyurethane based on MDI and 1,12-dodecandiol was prepared by a solution polymerization in DMSO (12). Polyurethane elastomers were prepared by a prepolymer method (13).

For obtaining the semi-crystalline and amorphous polyurethane films based on 1,12-dodecandiol, 0.1 g of sample was dissolved in 10 ml DMF by heating. The solution was placed in an aluminum dish (diameter 5 cm). Annealing was accomplished by evaporation of DMF while heating at 160 C for 30 minutes in a vacuum oven. Quenching of the polyurethane film was accomplished by raising the temperature of the semi-crystalline film above 200 C followed by quenching at room temperature. The segmented polyurethane elastomer films were cast on aluminum dishes from DMF. Photolysis of the films was performed with 300 nm lamps (Rayonet Reactor) for various time periods. The photolyzed samples were dissolved in hot DMF and the insoluble

gel was collected, dried in a vacuum oven, and weighed. The films subjected to fluorescence analysis were photolyzed with a Xenon lamp (150 watt)/monochromator combination) at 280 nm with 5 nm monochromator slit widths.

The wide-angle X-ray diffraction measurements were made with a Philips PW-1720 generator (Cu target). Fluorescence spectra were recorded using a Perkin-Elmer fluorescence spectrophotometer model 650-10S. The thermal transitions of the polymers were examined with a Dupont 910 differential scanning calorimeter. IR spectra were recorded on a Nicolet Instrument Corporation model 1200 S.

Results and Discussion

A polyurethane based on MDI and 1,12-dodecanediol can, depending on its thermal history, exist in either a semi-crystalline or an amorphous state. A semi-crystalline film of an MDI-1,12-dodecanediol polyurethane was obtained by casting the polymer from a dilute hot DMF solution followed by annealing for 0.5 hours at 160 C, well below its crystalline melting point. Both wide angle X-ray scattering and DSC analysis confirmed that the film was semi-crystalline with a melting point of 180 C. An identical film was subjected to heating well above its melting point followed by a rapid quenching at room temperature. The resultant quenched film was found to be amorphous by X-ray diffraction and DSC analysis. Both films, one annealed (semi-crystalline) and the other quenched (amorphous), were irradiated under identical conditions in a Rayonet Reactor (300 nm lamps) for various periods of time at 35 C, well below the T_g of either film. Although numerous spectral (UV/VIS, IR) and physical (brittleness, elongation, tensile strength, gel formation) measurements have been employed to evaluate the photodegradation of polyurethanes, for convenience we report only results of insoluble gel content as a measure of the extent of degradation (similar results are obtained by other measurements). Thus, Figure 1 shows that the extent of degradation of the photolyzed polyurethane (semi-crystalline and amorphous) films increases with photolysis time. The quenched (amorphous) film, for a given photolysis time, has substantially higher insoluble gel content. The semi-crystalline film is characterized by reduced flexibility which probably inhibits the chemical rearrangement processes leading to crosslinking and insoluble gel formation. The gel results are confirmed by the changes in the fluorescence spectra of the two films upon photolysis. The photolyzed amorphous film has a new red-shifted fluorescence spectrum (λ_{ex} = 280 nm) with peak maximum at 420 nm (Figure 2). The new emission may well be due to an ortho photo-Fries product. This is postulated on the basis of comparison with the emission maxima of alkyl anthranilates, e.g., the emission maxima of ethyl anthranilate in polyurethane matrices is 420 nm. Interestingly, the semi-crystalline film shows very little or no emission above 400 nm for a comparable photolysis time (Figure 3). These results (Figures 2 and 3) are consistent with the insoluble gel content data in Figure 1 and are especially attractive in view of the fact that one possible mechanism for gel formation in polyurethane systems is photolysis of an ortho photo-Fries product (or other products) generated by the primary photochemical reaction. In summary, both fluorescence analysis and gel content results lead to the conclusion that crystallinity plays an important role in the photodegradation process of a simple MDI based polyurethane.

Having explored a simple polyurethane system, we now turn to the more complicated segmented polyurethanes formed between MDI, 1,4-butanediol, and oligomeric polyols. In the first group of segmented polyurethanes investigated, the polyols employed were all based on poly(ethylene oxide) (PEO). The polyurethanes were synthesized by the standard 2 step method with 1,4-butanediol as the extender in each case. The ratio of MDI:1,4-Butanediol:PEO is 2:1:1 for each polymer. The polyurethanes are named according to the PEO molecular weight. Thus, the segmented polyurethane comprised of 2 parts MDI, 1 part 1,4-butanediol, and 1 part PEO (average molecular weight of 300) is PU-PEO 300. The other two polymers are named accordingly PU-PEO 400 and PU-PEO 600. Figure 4 shows results for photolysis of cast films (DMF solvent) of PU-PEO 300, PU-PEO 400, and PU-PEO

600. As the molecular weight of the PEO soft segment increases, the percent insoluble gel formed increases. How can these results be explained? One might first turn to a crystallinity argument. However, DSC and X-ray diffraction analysis of the three segmented polymers show little or no crystallinity. Consideration of the increasing flexibility of the soft segment on going from PU-PEO 300 to PU-PEO 600 might account for some difference in behavior, but the most compelling argument involves the dramatic difference in the nature of the hydrogen bonding characteristics of the three segmented polyurethanes under consideration. The FT-IR spectra of PU-PEO 300 and PU-PEO 600 (Figure 5) reveal a hydrogen-bonded carbonyl ($1,705\text{ cm}^{-1}$) and a non-bonded or free carbonyl ($1,725\text{ cm}^{-1}$) (see reference 14 for discussion of this phenomena). In the case of PU-PEO 300, there is a significant degree of hydrogen bonding to the carbonyl in the urethane moiety. PU-PEO 600 on the other hand has primarily non-bonded carbonyl and is free to move. PU-PEO 400 is intermediate between PU-PEO 300 and PU-PEO 600. This could well account for the lower yield of gel content on photolysis of PU-PEO 300 since the carbonyl radical formed by an N-C bond cleavage in the excited urethane group, if restricted by hydrogen bonding, might be less likely to lead to photodegradation. The hydrogen bonding argument, in general, calls for restrictive local mobility and as such would be expected to inhibit processes leading to crosslinking (gel formation).

In order to extend our study, a series of segmented polyurethanes based on MDI, 1,4-butanediol (BDO), and poly(tetramethylene oxide) (PTMO—average molecular weight 1000) were synthesized with varying hard segment content. Figure 6 shows that as the hard segment concentration increases (increasing 1,4-butanediol content) the extent of insoluble gel formed upon 8 hours photolysis with a Rayonet Reactor (300 nm lamps) decreases. The decrease in gel formation probably results from a decrease in polymer flexibility and/or an increase in hydrogen bonded carbonyl with increasing hard segments. Both factors should serve to restrict the degree of photoinduced crosslinking.

Conclusions

Results for photolysis of a simple polyurethane based on MDI and a single aliphatic diol (1,12-dodecanediol) and segmented polyurethanes based on MDI, an aliphatic diol (1,4-butanediol) and a polyol have been presented with emphasis on the effect of the physical structure of the film on the photodegradation process. In the case of the simple polyurethanes, crystalline content impedes the formation of insoluble gel. For the segmented polyurethane films, the degree of hydrogen bonding to the carbamate carbonyl moiety and/or the flexibility of the polymer chain can significantly alter the photodegradation process. Put into perspective, this work emphasizes the necessity for consideration of the physical state of polymers in the photolysis process. Extension of this concept to other polymer systems is in progress.

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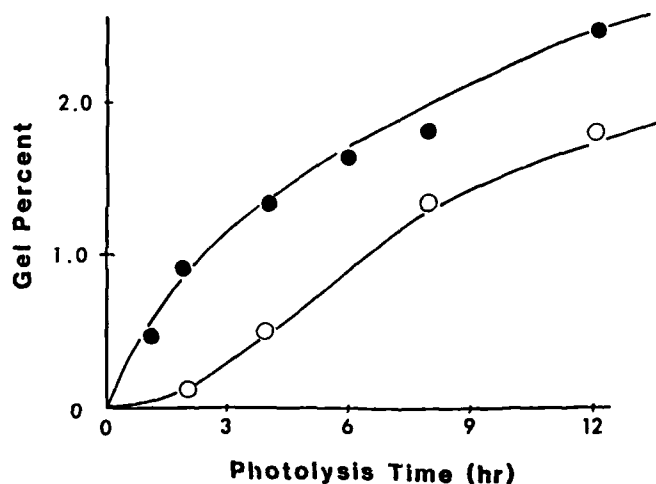


Figure 1. Insoluble gel formation on photolysis (Rayonet Reactor, 300 nm lamps) of MDI-1,12-dodecanediol polyurethane films. (a) Quenched amorphous film (filled circles). (b) Annealed semi-crystalline film (open circles).

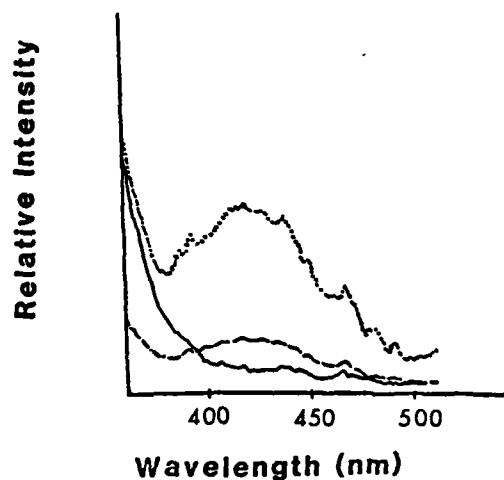


Figure 2. Fluorescence spectral change ($\lambda_{\text{ex}} = 280 \text{ nm}$) on photolysis (Xenon lamp/monochromator system for 20 minutes) of thermally quenched amorphous film of MDI-1,12-dodecanediol. (a) Before photolysis (b) After photolysis (x1) (c) After photolysis (x3)

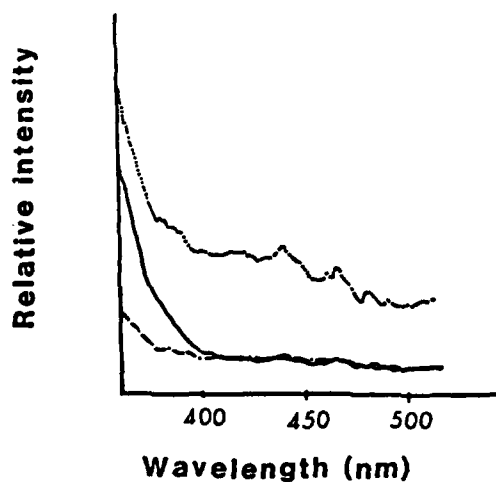


Figure 3. Fluorescence spectral change ($\lambda_{\text{ex}} = 280 \text{ nm}$) on photolysis (Xenon lamp/monochromator system for 25 minutes) of annealed semi-crystalline MDI-1,12-dodecanediol film. (a) Before photolysis (b) After photolysis (x1) (c) After photolysis (x3)

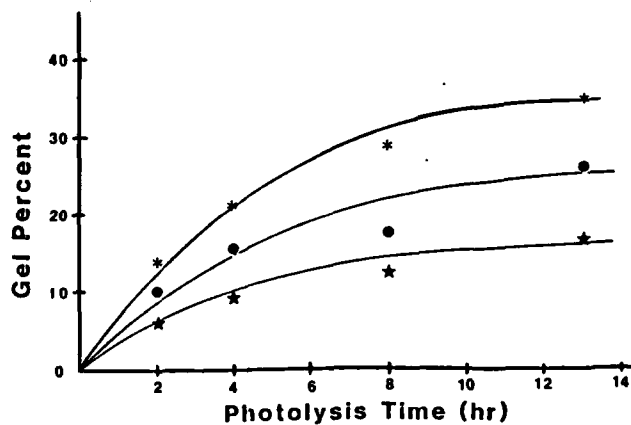


Figure 4. Insoluble gel formation on photolysis of segmented polyurethane films in Rayonet Reactor (300 nm lamps).
 (a) PU-PEO 300 ★★ ★★ (b) PU-PEO 400 ● ● ● ●
 (c) PU-PEO 600 * * * * .

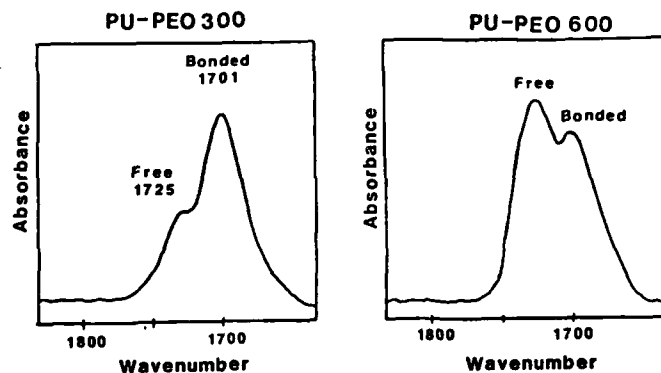


Figure 5. FT-IR spectra of PU-PEO 300 and PU-PEO 600 films.

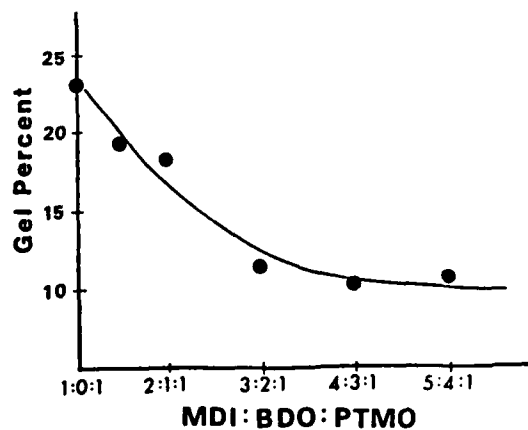


Figure 6. Insoluble gel formation on photolysis (8 hrs, Rayonet Reactor, 300 nm lamps) of segmented polyurethane films.

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